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CONTENTS

	Page
Editorials	1
Original Contributions:	
A Rapid Quantitative Method for Determining the Decolorizing Power of Carbons—*D. S. Chamberlain and M. K. Buckley*	4
A New Type of Color-Comparator—*H. S. Bailey*	8
The K. and E. Color Analyzer—*Carl W. Keuffel*	14
The Detection and Estimation of Small Amounts of Chromium in Fats—*A. O. Snoddy*	20
Action of Fatty Acids and Oils on a Photographic Plate—*W. F. Baughman and G. S. Jamieson*	25
An Apparatus for Approximate or Comparative Melting Points of Fats, Waxes and Petroleums—*Hoyt Stevens.*	28
Government Department Note	30
Obituary	31
Abstracts from Other Journals	31

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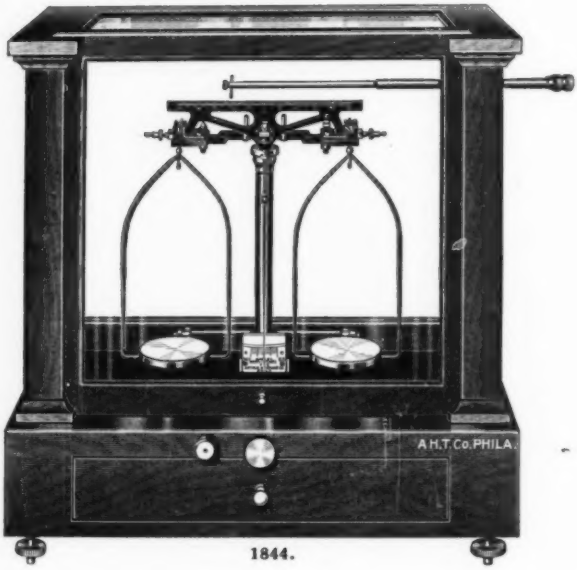

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Journal of Oil and Fat Industries

Devoted to Oils, Fats and Allied Industries

VOL. II **JANUARY, 1925** **No. 1**

EDITORIALS

A VISION FOR 1925

The past year was for many businesses and many men a discouraging one. Since the fall, however, with better crops, better general conditions and finally with our quadrennial depressant, the presidential election, out of the way, matters have so brightened that we can look forward confidently to the new year.

The A. O. C. S. has suffered loss and there are many gaps to fill, but with our organization intact and with the confidence and enthusiasm of its members undimmed there is nothing but a bright future ahead of us, a future of mutual help among our members and further assistance to all the oil and fat industries in which we are interested.

Our needs for the coming year are many. The greatest probably is the assistance of chemists not now affiliated with us. Our progress in any field of oil and fat technology depends largely upon those most interested in that particular field to help formulate methods acceptable under varying conditions, to originate new methods and research of basic and mutual character.

The past has given us confidence that with the same interest, the same mutual assistance and enthusiasm which have contributed to our successes applied to other particular lines wherein oils and fats are basic will make of the coming year 1925 a most successful, prosperous and happy one.

H. J. MORRISON

ALL-TOGETHER

Oneness of purpose, in the individual, the family, state or association spells success. If it is a letter in the morning mail or a suggestion from some one at the office that determines your task for the day you are not one of those men who are marked for great achievement. The opportunist

is not a go-getter. Progress depends upon purpose. It does not wait upon opportunity. Divine guidance is a great blessing but only he who is hitting the trail will pass the guide posts: They are fixed, he must move if he would find them.

Those interested in fats and oils, whether as investigators, technologists or producers have a common meeting ground. The paint man may learn from the soap man, the edible products man from him who makes only technical products, the emulsion manufacturer from the fellow who is lying awake nights trying to break emulsions. This common ground is our Society and its JOURNAL.

Oneness, collaboration, unity or the homely expression, pull together, whatever we call it, must prevail if we the oil chemists and technologists are to put our industries where they belong. New Year's Resolutions are the style this month. Shall we make ours All-together of Oils and Fats, or for brevity, just, "Oil-together." That should make things run smoothly.

H. S. B.

ANALYSTS vs. CHEMISTS

"What the chemical profession in America needs right now is a more general appreciation of the distinction between an analyst and a chemist." This statement was recently made by a gentleman who has had a very broad experience as routine analyst and later director of research in government laboratories, a teacher of chemistry in a university and chief chemist for a company where he had charge of eight or ten control and research units. He believes we should recognize that not all chemists are reliable analysts and also that many analysts have neither the theoretical training or natural temperament to make research men.

Has the chemical field become so broad that there are in it not merely different branches but different strata? To borrow from our paleontological friends a simile, must we distinguish between flora and fauna as well as between the carboniferous and the miocene? Is there an actual difference between those that would solve the structure of the atom or synthesize a new dye and they who day after day repeat the same, painstaking analyses that our bridge girders may be safe or our mill operations efficient?

It is recognized that machinists are rarely embryo mechanical engineers; electricians are not as a rule confused with electrical engineers, nor do the wages of carpenters or stone masons materially affect the salaries of architects or construction engineers. We American chemists, however, cloak all who use the wash-bottle and test-tube with the single appellation "CHEMIST."

Many executives know the personnel of their entire chemical depart-

ment merely as chemists. They recognize degrees of chemical ability but fail to distinguish between the "titer-boy" with only a common school education and the junior chemist just hired from a university. Services, like commodities, are largely evaluated by classes. If there are "Chemists" on the pay roll at sixty per month, even though they are well trained, not educated, routine workers, what chance has the new boy who has spent his own or his dad's good money for a college course to earn even the interest on his investment?

Our English colleagues have been worrying because in their land the druggist is commonly known as a Chemist. With them the title Analyst has also a somewhat different connotation from what it carries in the United States. When we distinguish between Chemist and Analyst we usually think of the former as college-trained men with a scientific education, and the latter as skillful users of analytical methods, workmen trained in laboratory technique. If a more general appreciation of the differences between a Chemist and an Analyst will add to the prestige of our profession, and raise the salaries of Chemists and not merely lower the pay of the Analyst, let's have it. Will it? That is the question. H. S. B.

DIVERSIFICATION

Since the Liberty Loan Drives and the subsequent conversion of good bonds into wild cat stocks, even we chemists have been favored with the broker's literature. One oft repeated warning to the prospective investor has been that he must have diversification in his holdings. The readers of these pages have before, and doubtless will again, have called to their attention the importance of diversification in their chemical reading.

The JOURNAL is endeavoring to supply such diversification, but apparently this issue has run largely to problems connected with the colors of oils, their evaluation or removal. In the next number, however, there will appear an article on the Digestibility of Fats, Some of the Economic Aspects of the World Trade in Oils, and a paper of especial interest to the linseed oil users and producers.

We still have room for more good papers, and will especially welcome contributions from college and research laboratories, whether submitted by members of our Society or others. H. S. B.

ORIGINAL CONTRIBUTIONS

A RAPID QUANTITATIVE METHOD FOR DETERMINING THE DECOLORIZING POWER OF CARBONS

By D. S. Chamberlin and M. K. Buckley

In the examination of various decolorizing carbons for water soluble and acid soluble content, ash, specific gravity, etc., it was found necessary to have some method that would give a comparison of the decolorizing power of the same carbon and of different decolorizing carbons. As all the various quick methods had an indefinite end-point, due to being masked or due to lag, iodine was considered as a solute in that it had a definite end-point for titration and could be determined quantitatively. The methods in use are dye methods and color measuring methods.

The dye methods depend on the use of a definite weight of some dye, as 2.0 g. of methyl violet dissolved in 600 cc. of alcohol and diluted to 2000 cc. with water. One gram of the carbon is weighed into a 300 cc. beaker and 50 cc. of water is added. The methyl violet solution is run into the beaker slowly from a buret and the solution is vigorously stirred. The appearance of a purple tinge in the foam indicates the end-point. This end-point should be permanent for two to five minutes. The result is expressed in terms of the amount of carbon required to decolorize 0.05 of methyl violet. A second method is the use of 0.05 g. of eosin scarlet in 1000 cc. of water. The decolorizing power is expressed by the number of cc. of eosin scarlet that are decolorized by 0.3 g. of carbon.

The dye methods are very inaccurate in that the end-point is covered by the presence of the carbon in the solution, the end-point is not permanent in the presence of the carbon and the size of particle is not taken into consideration.

The methods for measuring color are well presented by Sanders,[1] in that the color of the particular solution to be treated by a chosen carbon is measured for color before and after carbon treatment. These methods require a color-measuring instrument, which in most cases is not a part of the equipment of the ordinary laboratory. Also, the preparation of the carbon and the manipulation of the solution requires considerable time before the sample is ready for color measuring.

The work of J. W. McBain[2] and J. B. Firth[3] on adsorption of iodine in a solvent of benzene or chloroform offered a possible means to determine the decolorizing power of carbons by treating a standard aqueous solution of potassium iodide and iodine with carbon, and determining by means of a

[1] *Chem. & Met. Eng.*, **28,** No. 12.

[2] *Jour. Chem. Soc.*, **91,** p. 1683.

[3] *Trans. Faraday Soc.*, **16,** p. 434.

standard sodium thiosulphate solution the quantity of iodine adsorbed. This method as developed must be understood to express the decolorizing value of carbons for iodine solution, or its "Iodine Number."

The solutions used in this method are:

I. 0.2 N iodine-potassium iodide solution (iodine, 25.384 g. and 50.0 g. KI per liter).

II. 0.1 N sodium thiosulphate ($Na_2S_2O_3.5H_2O$, 24.832 g. per liter).

III. 0.1 N tassium dichromate ($K_2Cr_2O_7$, 4.903 g. per liter).

IV. Starch solution (25.0 g. per liter).

The sodium thiosulphate solution was standardized against 0.1 N $K_2Cr_2O_7$ and the iodine by the 0.1 N sodium thiosulphate. The method as developed for the determination of the decolorizing power is as follows.

The Method

A sample of carbon ground through a 300-mesh sieve is dried for five hours at a temperature of 105°C. Five-tenths gram of the sample, weighed accurately to within 1 mg., is placed in a 1 liter beaker and 490 cc. of distilled water and 10.0 cc. of iodine solution are added in the order named. This solution is stirred for 3 minutes and filtered through absorbent cotton. Two hundred and fifty cc. of the filtered solution is caught in a volumetric flask as a sample for titration with the 0.1 N thiosulphate solution, using, near the end-point, 0.5 cc. of starch solution and titrating to the first disappearance of the blue color. A blank is now run in the same way but using no carbon. The decolorizing power for iodine can be calculated by subtracting the $Na_2S_2O_3$ titration of the sample from that of the blank, e.g.,

$$\frac{\text{cc. } Na_2S_2O_3 \text{ equivalent to iodine adsorbed} \times 100}{\text{cc. } Na_2S_2O_3 \text{ equivalent to total iodine used (blank)}} = \% \text{ iodine adsorbed}$$

or the decolorizing value.

The proper weight of carbon to be used was determined by keeping all the variables constant and only varying the weight of carbon. As different

TABLE 1

VARIATION WITH WEIGHT OF DECOLORIZING POWER

Weight Carbon Grams	Carbon Number 1	2	3	Carbon Number 1	2	3
	Cc. $Na_2S_2O_3$			Per cent decolorizing power		
0.050	7.45	7.90	6.75	11.84	6.52	20.05
.100	6.45	7.55	5.50	23.70	10.65	34.95
.175	5.05	7.20	3.90	40.30	14.80	53.80
.250	4.10	6.50	2.80	51.50	23.07	66.90
.375	2.55	5.60	1.55	67.50	33.70	81.66
.500	1.50	4.75	0.75	82.30	43.75	91.20
.675	0.85	3.80	.30	89.90	55.00	96.45
.800	.55	3.25	.15	93.50	61.50	98.25
1.000	.30	2.50	.10	96.50	70.45	89.90
.....	8.45	8.45	8.45			

· Time, 3 minutes. Samples unprepared for size.

weights adsorbed different amounts of iodine, the results so obtained when plotting weight of carbon against per cent of iodine adsorbed show the "break" at the point where the value of the carbon axis is 0.5 g. (Table 1). It is evident that the curves tend to straighten out at the ordinate 0.5 g. and thereafter follow very closely the vertical ordinate. Firth[1] also pointed out this fact when he plotted log $\frac{x}{M}$ and log $(a\text{-}x)$ as derived from the adsorption equation of Freundlich, $\frac{x}{M} = BC\frac{1}{p}$, where x is the weight of the material adsorbed, c is the concentration after treatment, and B and p are constants.

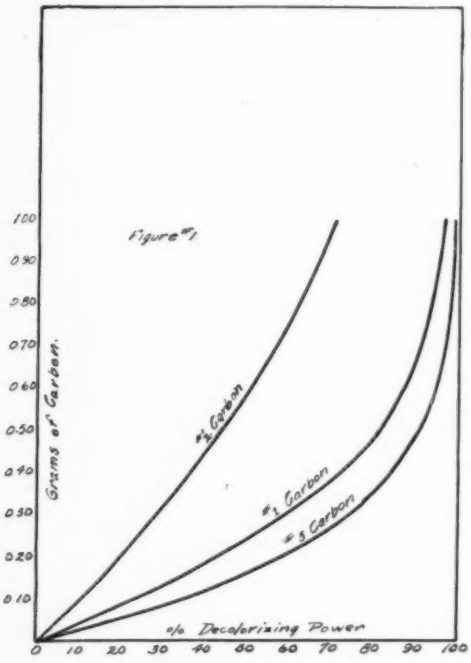

Fig. 1

By plotting the foregoing results according to the logarithmic equation, the curves from the ordinate 0.5 g. are straight lines. The value a is the weight of the total amount of solute used.

The size of the particles making up the sample is important, as the size of the particle determines the surface exposed for adsorption. To bring all the samples to a practical state of uniformity, relative to the amount of surface exposed, they should be ground to pass a 300-mesh sieve. The data in Table 2 show the decolorizing value of a carbon before and after grinding through 300 mesh, the time of adsorption being kept constant at 3 minutes.

TABLE 2

VARIATION WITH SIZE OF DECOLORIZING POWER OF NO. 1, CARBON

Weight Carbon Gram	Unground Cc. $Na_2S_2O_3$	300 mesh Cc. $Na_2S_2O_3$	Unground Per cent	300 mesh Decolor. power
0.500	2.40	1.75	77.66	82.50
.500	2.90	2.00	70.56	80.00
.500	2.65	1.90	73.09	81.00
.500	3.20	2.05	67.51	79.50
.500	3.30	2.60	66.49	74.00
.500	2.50	1.95	74.62	80.50
....	9.85	10.00		

[1] Firth, *Loc. cit.*

Naturally if one is using the same carbon at all times and wishes to check up the relative decolorizing values of various lots from the manufacturer, a fairly good comparison can be made without reducing the samples to a uniform size.

In order to determine the time for iodine adsorption the weights were varied and the time of agitation held constant for 3 minutes, 6 minutes and 9 minutes. The time data in Table 3 show a very small and practically constant difference in the rate of the thiosulphate titration after the second 3-minute agitation period.

O. C. M. Davis[1] states that the surface condensation is nearly instantaneous and is quite complete in a few hours: the diffusion (capillary absorption) proceeds for weeks, months and even years.[2] To check our results on "time," the 3-minute period was overrun a minute with and without stirring, no change being found in results.

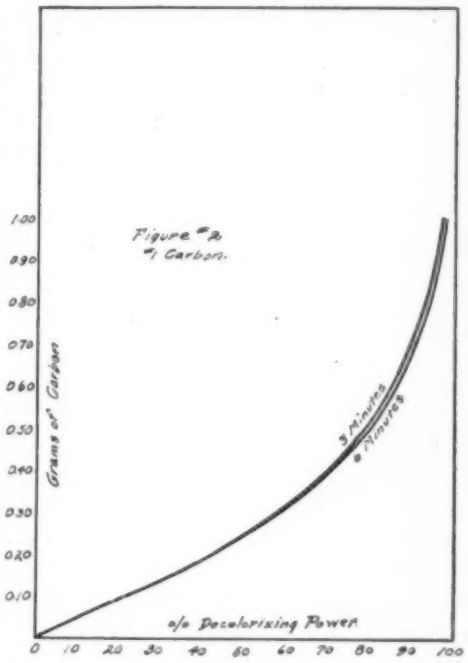

Fig. 2

The temperature is not important if the entire manipulation is carried on at room temperature, as the running of the blank allows for the correction of

TABLE 3

VARIATION WITH TIME OF DECOLORIZING POWER, OF NO. 1 CARBON

Weight Carbon Gram	Minutes Treated 3	6	Difference in $Na_2S_2O_3$ titrations	Minutes Treated 3	6
	Cc. $Na_2S_2O_3$			Per cent Decolor. power	
0.050	8.80	8.55	0.25	10.66	10.94
.100	7.80	7.60	.20	20.81	20.83
.175	6.20	6.00	.20	37.05	37.50
.250	5.00	4.80	.20	49.24	50.00
.375	3.50	3.30	.20	64.77	65.62
.500	2.05	1.95	.10	79.19	79.69
.675	1.15	1.00	.15	88.32	89.59
.800	0.75	0.60	.15	92.39	93.75
1.000	.30	.20	.10	96.95	97.92
....	9.85	9.60	.25		

[1] *Jour. Chem. Soc.*, **91**, p. 1666.

[2] *Loc. cit.*

any small amount of iodine that will volatilize. Nevertheless, dispatch in manipulation should be exercised to cut any possible loss to a minimum, due to the volatility of the iodine. From the initial weighing of the sample to the final titration, a maximum time of 10 minutes should suffice.

Conclusions

1. This method is a rapid quantitative method for the determination of the decolorizing power of carbons for iodine.
2. The method can be used for controlling the plant output of any one kind of carbon without a size preparation.
3. The method can be used for comparing decolorizing carbons manufactured by different methods.
4. The adsorption for iodine is practically instantaneous.

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A NEW TYPE OF COLOR-COMPARATOR

BY HERBERT S. BAILEY

History of Oil Colorimetry

Not so many years ago, the determination of the color of oils, in the cottonseed oil industry, was of minor importance, but when this factor was introduced into the trading specifications it soon became necessary to have some basis upon which to report colors. The earliest of these standards was probably bichromate of potassium solutions made up in definite concentrations. It was soon found, however, that such solutions did not simulate the color of refined cottonseed oils sufficiently to prevent grave disagreements between the buyers' and sellers' analysts.

The next step was perhaps the adoption of the Lovibond glasses and these are still in almost universal use, by American oil chemists. They have not, however, proven entirely satisfactory. Much time and energy have been given by members of the American Oil Chemists' Society, to finding some means for bringing about better agreement between their color readings. These studies have followed two distinct lines; the development of a new type of color comparator or a simple spectrophotometer; and refinements in, or more specific directions for, the use of the Lovibond glasses. Dr. Priest of the U. S. Bureau of Standards has most generously aided in devising a new color instrument and it is largely as a result of his work, that the E-K Color Analyses described elsewhere in this issue of the JOURNAL, has been placed on the market. Dr. Wesson in 1920 enlisted the assistance of the Eastman Kodak Company in the problem and they built, for a number of oil laboratories, a very convenient type of color comparator. This instrument is quite expensive and has the added disadvantage that its

readings are in a new terminology which is unintelligible to the refiner and trader. Recognizing the difficulties in the way of getting the oil trade to adopt an entirely new basis for color readings, Dr. Wesson and others have studied the causes for the lack of agreement which exist, when different analysts determine the color of oils with the Lovibond glasses. A bibliography of the papers which have appeared in the Chemists' Section of the Cotton Oil Press and this JOURNAL, is appended for the benefit of those who may be interested in perusing further the history of the Society's work on color standards. It was largely due to previous investigators' work that the author was led to attempt the design of an instrument which he hoped would eliminate the variables in Lovibond readings and permit of our continuing to grade oils on this scale. To accomplish this, we must first bring the individual chemist's color reports on all oils into sufficiently close agreement so that the trade will no longer have occasion for complaint.

Causes for Lack of Uniformity in Lovibond Readings

There are several more or less obvious reasons why in the past different laboratories have not agreed on the color of oils when these were read against Lovibond glasses. Some of these are inherent in the glasses themselves, others cannot be eliminated by any scheme which depends upon the color sensitiveness of our eyes. It is difficult to find any two persons who will match identical colors of different substances, in this case, oil and glass, exactly the same. To eliminate this personal equation, we must go to a color analyzer, not a color comparator. There are, however, several factors, such as the light source, its intensity, and the method of combining the Lovibond glasses, which may be made uniform in all laboratories. It is by the fixing of these variables, together with a standardization of the glasses in all instruments that we hope to bring about a satisfactory harmony in color readings.

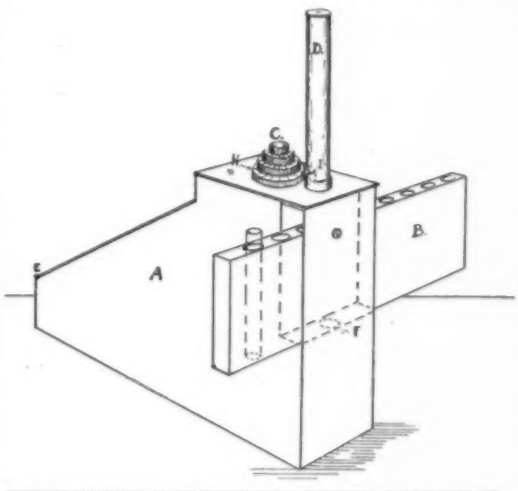
The work of Priest and his collaborators has demonstrated that Lovibond glasses of the same number are not always of identical color, also that the scale is not strictly additive, by which we mean that three number 5 red glasses piled on top of one another are not exactly equivalent to the number 15 glass. Therefore, all laboratories must either have a full set of glasses, or use the same combinations for producing shades for which they have no single glass. Only by adopting as a color basis a properly standardized set of glasses, can the errors in the glasses themselves be obviated. Such a set of thirty-two glasses is now being compared with the U. S. Government's standard Lovibond scale. Should it become the property of the A. O. C. S., as is most likely, we will have available a basic standard against which can be checked the glasses in our laboratory instruments.

In the device, which is here proposed, a nearly standard light source, consisting of a 75-watt Mazda lamp and Eastman Kodak Company's daylight filter, is used for all color readings. The 32-Lovibond glasses are so arranged in suitable carriers that all colors from zero red—zero yellow to 39 yellow—10.9 red, can be made by the combination of four glasses, including the colorless ones, and always four glasses must be in the optical field. Thus in every reading there are the same number of reflecting surfaces which tends to keep the light intensity uniform. In this connection one should remember that in passing through glass, light is lost, not so much by absorption within the glass, as by reflection at the incident and emergent surfaces. Since the range of colors required in matching all ordinary cottonseed-oils, both refined and bleached is covered by the 32-Lovibond glasses and four clear slides, the use of the "fractional" glasses such as 7.6 red, is eliminated. The glasses are combined on the decimal system similar to the weights on an analytical balance: All the red tenths are in one carrier, and the units in another. Thus to make a red reading of 7.6 one must use the 7 and the 0.6 glasses and cannot obtain 7.6 red by any other possible combination. Similarly the "yellows" are in two carriers, those from 1 to 9 inclusive in one, and a 10, 20, 30 and 35 in another. To match a 22 yellow oil the 20 in one carrier and the 2 in the other are superimposed in the optical field. For convenience in reading refined oils a 35 yellow glass has been included in the device. This does make possible the setting up of the yellow values between 35 and 39 with two different combinations. For instance 37 might be made either with the 30 and the 7 or the 35 and the 2. Whether or not this inclusion of a 35 yellow glass is advisable, remains to be seen. If it is used only for 35 yellow oils and those darker than 39 there will be no danger of different operators getting different readings, if, however, some do not follow this scheme, then it were better to omit the 35 yellow and forego the slight convenience which its inclusion in the set occasions. For reading oils darker than those within the range of the 32 glasses, provision has been made for inserting in the optical field additional glasses. This will be explained more fully in the description of the instrument. Minor but added advantages in the proposed device, over the old manual method of handling the glasses, is that they are protected at all times from dirt and scratches and the value of the glasses is read directly from dials instead of paper labels all too often almost illegible.

Description of B-L Color Comparator

The new colorimeter, or color comparator as it should perhaps be called, is shown in the accompanying figure. It consists of a metal box (A), a rack for the standard color tubes (B), a series of four super-

imposed circular plates, carrying the color glasses and provided with suitable nurled heads for turning (C), and a sight tube or telescope (D). The box proper which is the housing for the light, color glasses and guide for the tube holder is a sheet iron affair finished outside in black enamel and inside in matt black. It is mounted on a suitable base and the entire appartus is self-contained and occupies a table space less that two feet square. The 75-watt Mazda lamp, which in the standard light source, is held in a horizontal position by a porcelain, pull-chain socket inserted through the back of the box near the bottom. At the front end of the box is a 45° platform upon which is placed the block of magnesia that reflects the white light through the oil and the color glasses. A large cover hinged (E) at the back, closes the sloping portion of the box and permits of easy access to the light and the magnesia block. The upper one and one-half inches of the box is separated from the lower part by a partition which forms a dust-tight compartment for the color-glasses in their carriers. The only hole in this compartment is one for the admission of light to the glasses and this is made dust-tight by a piece of clear microscope slide.



New color comparator

To facilitate the handling of a number of samples of oil at one time, the rack (B) is made to hold ten regular $^3/_4'' \times 6''$ color tubes. This rack is of monel metal, with a brass-bottomed plate the holes in which are tapered and so shaped as to center the tubes automatically between the four small points that support them. This gives an unobstructed view through the entire bottom of the tube which is always in the center of the optical field irrespective of slight variations in its diameter. The tube rack slides in a narrow gallery across the front end of the instrument box and rests upon the floor of this gallery. The hole (F) through the floor which admits the light to the oil column is covered by a microscope slide which prevents oil and dirt from getting down onto the magnesia block immediately below it. This slide is readily removed from the inside, for cleaning when necessary. As a convenience in filling the tubes with oil to the proper depth, the rack is made of such

a height that when the bottom of the meniscus of the oil in a tube in place can just be seen across the top of the rack, one has a $5^1/_4$" column. Opposite each tube along the face of the rack is a number, in white, which appears through the hole (4) in the front panel of the instrument when the corresponding tube is centered beneath the telescope. Any number of racks can of course be provided and if they be serially lettered, one can prepare a large number of oils for reading, then run them through the instrument much as magazines of shells are passed through a rapid fire gun. The top of the box is a solid brass plate from which is supported the mechanism for holding the Lovibond Glasses and turning them into the field of vision as desired. The boss in which is fitted the observation tube or eyepiece is also a part of this top casting which is fastened by small screws to the box and by removing these, one can easily get, at the color-glass carriers, should that be necessary.

A full description of the device which holds the glasses would be difficult without a more detailed drawing than the one here shown. It consists of four cast brass disks, each fastened to a thick cylindrical ring. The upper ends of these cylinders, the center one of which is a solid rod, project above the cover as shown at (C). Upon their top surfaces are engraved the values of the glasses and sector lines in such a manner that when one looks directly down upon them he sees four concentric dials each divided into eleven, numbered spaces. The numbers on the dials are directly opposite the corresponding glasses and thus the value of the combination in the optical field appears as a vertical row of four figures opposite the white arrow at the back of the top plate, as shown at (H). Since the darkest yellow glasses, the tens, are on the outer circle, the unit yellows next, then the unit reds and lastly the tenths on the center knob, one reads a color as he would add a column of figures. Thus for 22 yellow, 2.2 red, 20 yellow is farthest from him as he stands at the front of the instrument, then 2 just below, making the 22 yellow, next 2 red and on the center or nearest dial 0.2 or 2.2 red.

The observation tube or telescope (D) carries in the eye-piece a blue filter which gives with the 75-watt gas-filled, electric bulb a practical equivalent of normal daylight. This same result might of course be obtained by using a so-called "daylight" globe as the light source. It is believed, however, the filters will be more uniform, as they are the product of a reliable optical manufacture, and not subject to the change which takes place with all electric bulbs as they begin to burn out.

Near the bottom of the telescope is a slot (I), previously mentioned, into which may be inserted additional glasses when needed for matching very dark oils. As the tube makes a slip-joint with the boss which supports it, the slot can be turned either to the back or front, pulled up above the boss or pushed down to close the opening. When at the

back it permits of glasses being placed only over the field through which is viewed the color glasses. When at the front, standard glasses can be inserted over the field in which the oil is usually viewed, and if there be no oil below this field a direct comparison between the standard glasses and those in the instrument may thus be effected.

Summary

A convenient form of instrument has been devised for comparing the color of cottonseed oils with glasses of the Lovibond scale.

In this apparatus each color must be made up by a combination of the same color glasses, one chemist cannot use a single 8.5 red glass and another a 5, a 3, and a 0.5 glass to get the 8.5 match, all are forced to use an 8 and a 0.5 red, superimposed for this 8.5 reading.

The glasses are protected from dirt and scratches, and are easily revolved into the optical field by the turning of external nurled wheels.

The total color, yellow + red, when a match is made, is indicated in a straight vertical line upon four concentric dials, thus diminishing the chances for error in recording the glasses used.

A uniform light source, practically normal daylight, is provided in the instruments which will eliminate lack of agreement between different laboratories due to the use of various kinds of illumination.

The author wishes to express his indebtedness to Mr. P. F. Ballenger formerly Chief Engineer of the Southern Cotton Oil Co., for his assistance in solving the mechanical difficulties incident to the building of this device, for without his help it would be merely a chemist contraption instead of a finished instrument.

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SAN DIMAS, CALIFORNIA

THE K. AND E. COLOR ANALYZER

BY CARL W. KEUFFEL

The K. and E. Color Analyzer is a practical direct reading Spectrophotometer. It is used for determining the spectral transmission curves of all transparent substances, liquid or solid, such as colored solutions, oils, glass, etc., also for determining the spectral reflection curves of solid substances such as paper, soap, flour, etc. These curves can then be used to form the basis for a system of color specification or color control.

1. Spherical Light Source.
2. Photometer.
3. Spectromter.
4. Wave Length Scale.
5. Photometer Scale.
6. Holder for Staudard Sample.
7. Holder for Reflection Samples.
8. Holder for Transparent Samples.
9. Field of View thru Eye Slit.
10. To Vacuum Ventilator.
11. Plug for Vacuum Ventilator
12. 400 Watt Lamps.
13. Lever for Raising Photometer.
14. Sector Discs.
15. Universal 110 Volt Motor.
16. Speed Control Rheostat.
17. Entrance Slit.
18. Collimator Objectives.
19. Dispersion Prism.
20. Bi-Prism.
21. Eye Slit.
22. Cast Aluminum Base.

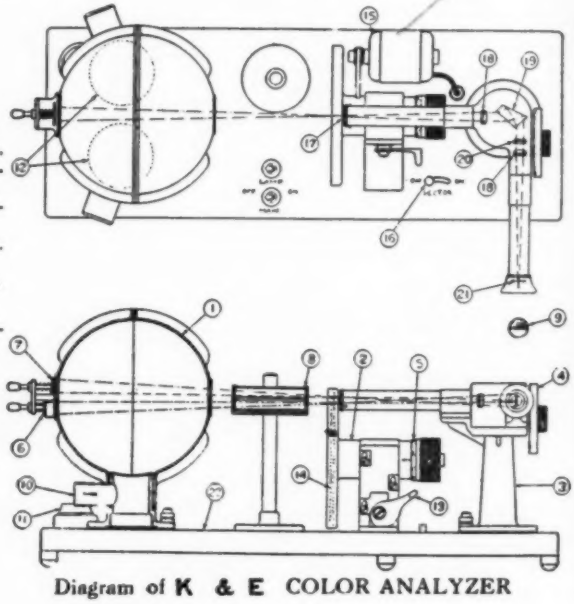

Diagram of K & E COLOR ANALYZER

Fig. 1

The Instrument consists essentially of (see Fig. 1);

A. The Constant Deviation Spectrometer (3) with its wave-length scale (4).

B. The Direct Reading Rotating Disc Photometer (2) with its photometer scale (5).

C. The Light Source (1) with its holder (6) and (7) for the samples when reflection measurements are made.

D. The stand with adjustable holder (8) for transparent substances.

When measuring a transparent liquid such as cottonseed oil, the sample contained in a glass tube of the desired length is placed in the holder (8) so that light from the upper beam passes through the tube of liquid. Two glass end plates are placed together on one end of an empty tube with a drop of the oil between them and this tube is placed in the path of the lower beam. This is done to make the instrument read directly the transmittance of the oil, and cancels the effect of the glass end plates of the tube or cell. The two beams then pass through the sector (14) which controls their relative intensity. This is done by turning the nurled head to whicht he photometer scale (5) (reading directly in per cent) is attached. The light from the beams then passes into the spectrometer where the beams are dispersed by the prism (19) into a spectrum. By turning the drum, to which the wave-length scale (4) is attached, any part of the spectrum can be selected and brought into the divided field for comparison. If we now analyze the colored light transmitted by the oil with respect to the relative amount of light of each wave-length in the spectrum, we will have the spectral transmittance of the oil.

An oil appears colored by transmitted light because it has the property of selective absorption or transmittance. This is a property inherent in the oil itself, and it is this property which we are concerned in measuring. When the light which has been transmitted by the oil impinges on the retina of the eye, it stimulates the optic nerve and produces the sensation of color. This sensation is not the same for any two observers because it depends upon the physical state of the observer's eye.

We are concerned with the measure of a certain *property* of the oil and not with its *effect* on an observer, *i. e.*, we wish to measure the *stimulus* which produces the sensation and not the *sensation* itself. The Color Analyzer measures this stimulus directly and absolutely. Its readings are independent of the color vision of the observer's eye, *i. e.*, a color-blind person will get the same results as a person with normal color vision. This is not the case with a "Colorimeter" which we may define as an instrument by means of which the observer adjusts a stimulus (under given conditions and limitations) to evoke a color matching the color being tested. Usually this adjusted stimulus is not identical with the actual stimulus of the color to be matched. In such a procedure different observers may obtain systematically different results according to the differences in the color vision of each. This is characteristic of all types of "Colorimeter."

When a colored object is viewed by the same observer but under lights of different quality (sun light, light from carbon lamp, light from tungsten lamp, etc.) the sensation produced under each light will be different, and

the color of the object, although it has not changed physically, will appear changed to the observer. Measurements made with a "Colorimeter" therefore are dependent on the light source with which the sample to be measured is illuminated. Measurements made with the Color Analyzer, however, are independent of the quality of the light source.

The following is a quotation from I. G. Priest (*Trans. I. E. S.*, Vol. XIII, No. 1, p. 413).

"Of whatever value the so-called 'Colorimeter' may be in special cases, it must be admitted that the fundamental basis of color specification is spectrophotometry."

While it has long been recognized that the spectrophotometer is a requisite in color work, providing, as Mr. Priest says, the fundamental basis of color specification, the only spectrophotometers hitherto available have been highly scientific instruments so elaborate in design, expensive in original cost, and so difficult to set up and to operate as to place them beyond the pale of the ordinary laboratory.

H. E. Ives (*Journal of the Franklin Institute*, Dec., **1915,** p. 700) says: "A spectrophotometric table derived from at least 25 points (for a continuous spectrum) gives the only unique description of a color, and it appears probable to the writer that the requirements of precision technical color measurements are most likely to be met by the development of simple and rapid means of plotting and recording accurate spectrum plots of reflection or transmission characteristics." The K. and E. Color Analyzer was developed to meet this need and has been in practical use in many of the industries for over two years.

Mr. I. G. Priest has for some years advocated the method of spectrophotometric analysis for specifying the color of cottonseed oil. His researches in this field have shown that oils can be accurately graded by this method. The time taken to make a measurement depends upon the number of points necessary to determine the curve properly. In order to determine exactly how few points on the transmittance curve would still properly specify the color, further research would be necessary. It has been found, however, that the transmittance curves of various cottonseed oils have their maxima and minima at the same wave lengths (see Fig. 2) and this suggests that readings at the following wave lengths, 540, 590, 610, 635, 670, 700, would be enough to specify the color of the oil. It may be difficult to visualize the color represented by six such readings, but it is possible to compute from these readings a single value (expressed in wave length) for the *quality* of the color and another value for the *brightness* (expressed in per cent). These two numbers give an exact description of the color which can with some experience be easily visualized. In Fig. 3 the transmittance curve for the cottonseed oil is 1 and the transmittance curve of the Lovibond glasses which match this oil is 2. The

numerical value for quality of the color of the oil is 583.2 and for the glasses is 581.8. The value for brightness is 1 = 28.5%, 2 = 28.9%. This example was taken from an article by Priest on the "Relations between the Quality of Color and the Spectral Distribution of Light in the Stimulus." There are other ways in which the spectral distribution curve can be changed to a simple notation of three numbers which will exactly represent the curve and which can easily be visualized as a color.

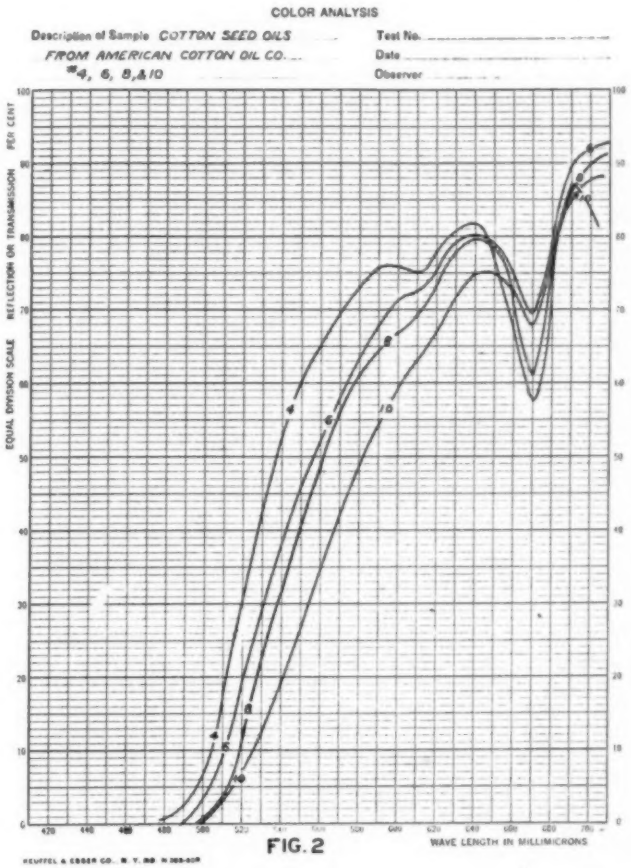

FIG. 2

The three curves A1, A2, and A3, shown in Fig. 4 indicate another useful purpose to which the measurements made on the Color Analyzer may be put. These curves show the cottonseed oil A1 before bleaching, A2 after bleaching and A3 after deodorizing. The measurements prove that the processes through which the oils were put have taken out the absorption bands which showed in the unbleached oil. A study of the transmittance curves taken at various stages of a refining process could be made to

determine the efficiency of the process and may suggest methods for improving the process.

It is probably true that the K. and E. Color Analyzer seems unnecessarily elaborate and expensive for grading cottonseed oils, yet we have found that unless an instrument is well designed and manufactured it cannot be made to give the accurate results which are necessary in color measurement.

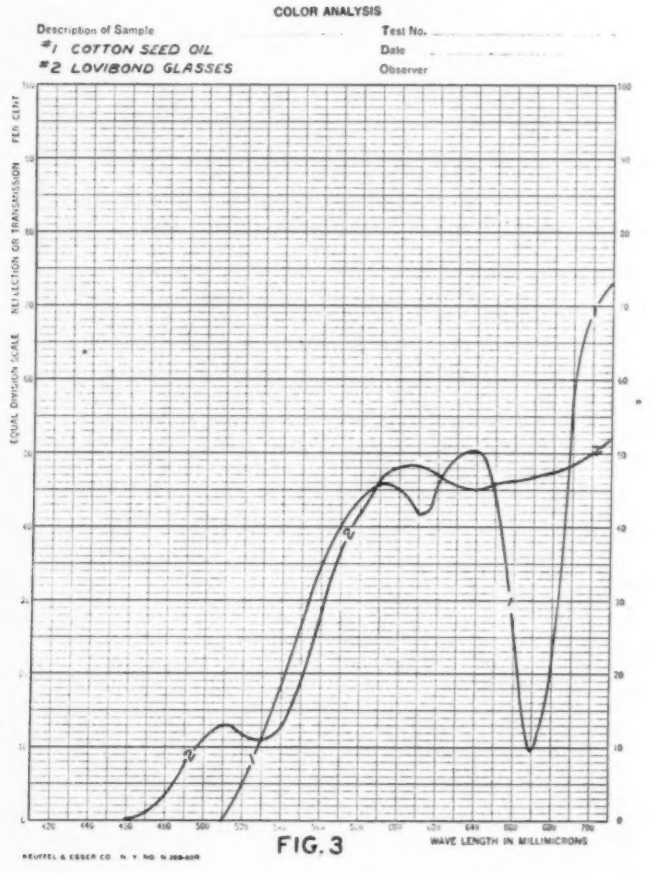

FIG. 3

The fact that the samples of oil are in a closed tube makes them easy to label and handle, especially when a large number of tests have to be made. The readings can be taken by inexperienced observers since no skill in color matching is necessary. The instrument is not limited to the measurement of transparent substances, but will equally well measure the color of solids or other substances such as pressed cottonseed cakes. Wherever the K. and E. Color Analyzer has been purchased for a certain problem, it was quickly found that it could be equally well used for other problems

which were not thought of at the time of purchase. It is impossible to predict what improvements we may be able to make as soon as we can accurately measure a quantity. In this connection it is fitting to call to your attention the following quotation from Parsons:

"We understand now that practically all we have mastered in science is what we have been able to measure or weigh."

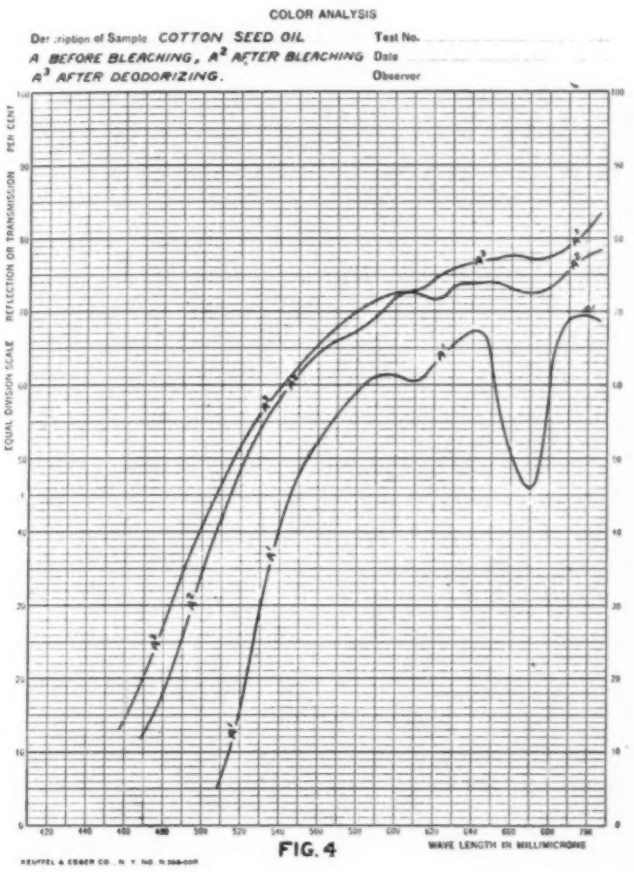

FIG. 4

In conclusion the outstanding features of this method of color measurement may be summarized as follows:

a. We can exactly specify a color by measuring its stimulus with the K. and E. Color Analyzer.

b. That this measurement is independent of the color vision of the observer.

c. That it is independent of the light with which the sample is illuminated.

d. That in the case of cottonseed oils it will probably be sufficient to determine only 5 or 6 points on the curve.

e. That it is possible to compute from the curve a single value for quality and one for brightness, which together give a simple system of notation for color. Aside from this, other methods of notation using three numbers are also available.

f. That the spectral transmittance curves may be useful in studying the efficiency of the bleaching and refining processes.

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THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF CHROMIUM IN FATS

BY A. O. SNODDY

It frequently happens that it is desirable to know whether a fat has been bleached by means of chromic acid and how much, if any, chromium has been left in the finished product made from such a fat.

Fats which have been bleached by chromic acid, even after refining and treatment with fuller's earth and repeated filtration, almost invariably contain small amounts of chromium, the persistence with which the chromium remains with the fat being due perhaps to its being present as a chromium soap, which is either actually soluble in oil or else so thoroughly protected by an oil coating that it escapes caustic refining and clarification treatments. The amount of chromium left in the fat will depend to some extent upon the care with which the treatments subsequent to the chromic acid bleaching are carried out and varies from a few hundredths to one or two parts of chromium per million of fat.

Advantage may be taken of the fact that dichromates react with symmetrical diphenylcarbazide, to give an intensely colored compound, to determine small amounts of chromium in the ash from such a fat. In the course of his work with phenylhydrazine E. Fischer[1] obtained phenylsemicarbazide and diphenylcarbazide. Skinner and Ruheman[2] obtained diphenylcarbazide by heating one mole of ethyl carbamate with two moles of phenylhydrazine until ammonia was no longer evolved. They also used urea instead of ethyl carbamate, this being considered at present the most efficient way of preparing this compound. They noted that mild oxidizing agents such as $CuSO_4$ and $HgCl_2$ gave colored compounds with diphenylcarbazide, and gave this as one of the differences between carbamide and those substances which contain groups of two atoms of nitrogen directly connected. They proposed this reaction with copper sulfate as a qualitative test for copper and showed that thiocarbazides also gave

[1] *Ann.*, **190,** 113 (1877); *Ann.*, **263,** 272 (1891); *Ber.*, **22,** 1935 (1889).

[2] *Ber.* **20,** 3372 (1887); *J. Chem. Soc.* (London), **53,** 551 (1888).

characteristic colors. Aside from $HgCl_2$ no other reactions with salt of metals are mentioned.

In 1900, M. P. Cazeneuve[3] reported the results of his investigation on the reaction between metals and their salts with diphenylcarbazide. His diphenylcarbazide was made by heating together phenylhydrazine and urea and purifying by crystallization from acetic acid or acetone. The reaction of metallic sodium, potassium and mercury and salts of mercury, copper, chromium, iron, lead, manganese, zinc, gold and silver are described.

Cazeneuve is of the opinion that in these reactions the diphenylcarbazide is oxidized to diphenylcarbazone which then reacts with the metal present to form an organo-metallic compound. Alcoholic sodium or potassium hydroxide reacts the same as the metals as indicated by these formulae.

$$O=C\begin{matrix}NH-NH-C_6H_5\\NH-NH-C_6H_5\end{matrix} + KOH \longrightarrow O=C\begin{matrix}NK-NH-C_6H_5\\N=N-C_6H_5\end{matrix} + H_2O + H_2$$

$$O=C\begin{matrix}NH-NH-C_6H_5\\NH-NH-C_6H_5\end{matrix} + H_2 \longrightarrow O=C\begin{matrix}NH-NH\\NH_2\end{matrix} + C_6H_5NH_2$$

No hydrogen is liberated as the nascent hydrogen is rapidly taken up by the diphenylcarbazide to form phenylsemicarbazide and aniline. The potassium salt of diphenylcarbazone can react through double decomposition with the salts of many metals.

Diphenylcarbazide may also react with salts of metals directly according to the following equation:

$$O=C\begin{matrix}NH-NH-C_6H_5\\NH-NH-C_6H_5\end{matrix} + 2Cu(C_2H_3O_2)_2 \longrightarrow O-C\begin{matrix}NCu-NCu-C_6H_5\\N-N-C_6H_5\end{matrix} + 4C_2H_4O_2$$

The highly colored organo-metallic compounds formed are in general unstable in the presence of acid, so that the reaction must take place in neutral or only faintly acid solutions. The chromium compound is an exception to this, being stable in concentrations of acid which do not permit the formation of a compound with other metals. This chromium compound gives a violet color to its aqueous solution which possesses such a tinctorial power that one part of chromium per million of solution may be easily recognized.

In 1906, Brandt[4] described a method for the analysis of iron based on the oxidation of ferrous to ferric iron by means of dichromate, using diphenylcarbazide as an inside indicator. Later, in 1913, Barnebey & Wilson[5] examined Brandt's method and were not able to obtain concordant results through its use in the analysis of iron. This they found to be due to

[3] *Bull. Soc. Chem., 3rd Ser.*, pp. 592, 701, 769 (1900).

[4] *Z. Anal. Chem.*, **45**, 95 (100).

[5] *Jour. Am. Chem. Soc.*, **35**, 156 (1913).

the fact that Brandt seems to have overlooked the fact that diphenylcarbazide consumes dichromate so that the amount of indicator used must be taken into account and a correction made for it. They found that each mole of potassium dichromate was equivalent to 1.5 moles of diphenylcarbazide and advanced the following equation "for the lack of a better one at the present time."

$3C_{13}H_{14}N_4O + 2KCr_2O_7 + 16HCl — 4CrCl_3 + 4KCl + 14H_2O + 4C_{13}H_{10}N_4O$

They believe that side reactions occur, and think the correction for the indicator should be made on a blank rather than through the use of a factor taken from the equation. When correction is made for the dichromate consumed by the indicator they find this a good method for the analysis of ores and other materials for their iron content.

Scott[6] describes a method for detecting and estimating small amounts of chromium by means of diphenylcarbazide.

Procedure.—200 grams of the fat to be analyzed for chromium are burned in a platinum dish. It is not necessary that the dish be large enough to hold the entire charge at once, a dish capable of holdng 40 to 50 cc. will suffice. The portion of the charge placed in the dish is heated over a gas burner until the oil takes fire, when the burner is removed and the oil allowed to burn quietly. As the oil is consumed, fresh portions may be added from time to time until it is all burned. A residue of coke is always left after the fat has burned, which is best reduced to ash by placing the dish in a muffle furnace, as small losses almost invariably take place when the coke is ashed over a free flame, due to draughts blowing some of the ash out of the dish. If a muffle furnace is not available the coke may be ashed over a flame, taking precautions not to lose any of the ash. Losses as great as 10% of the ash may easily occur if great care is not used.

Five grams of a mixture of sodium and potassium carbonates (equimolecular mixture) are placed on the ash in the dish and the mixture heated to fusion, the fusion being prolonged until any Cr_2O_3 which will be present in the ash of a fat containing chromium is converted to chromate. When this conversion is complete, the mixture is allowed to cool, the melt taken up in distilled water, made faintly acid with hydrochloric acid, and the solution made up to known volume in a calibrated flask. For amounts of chromium equivalent to about one part per million of fat a 50 or 100 cc. flask may be used, while for larger amounts 250 or 500 cc. flasks are convenient.

In the meantime a standard solution of dichromate is prepared; one which contains the equivalent of 0.000001 g. of chromium per cc. is a convenient concentration. This solution is made by weighing accurately

[6] Scott, "Standard Methods of Chemical Analysis," 3rd Edition, Vol. I, p. 163.

any convenient amount of C. P. potassium dichromate, dissolving it and making it up to volume, with water, in a calibrated flask, from which an aliquot part is further diluted with water in a second flask. This process is repeated until a final aliquot has been removed, which, when made up to its proper dilution with water, will be of the required chromium content. Before the final dilution is made, 5 or 10 g. of the mixed sodium and potassium carbonates—depending upon whether the dilution is to be 250 or 500 cc.—dissolved in part of the water to be used, are added to the flask. Enough HCl to make the solution slightly acid to litmus paper is added and the mixture made up to the proper dilution with distilled water.

This solution will contain sodium and potassium chlorides in about the same concentration as those resulting from the solution of the product of the ash fusion. The concentration of the chlorides, however, seems to have no important bearing on the reaction between the dichromate and the diphenylcarbazide or upon the color of the solution obtained from the reaction. For this reason nothing is gained by weighing the carbonates for the fusion or the standard solution more accurately than to the first decimal place.

A solution of diphenylcarbazide is made by dissolving 0.1 or 0.2 g. diphenylcarbazide in 10 cc. of glacial acetic acid and diluting this solution to 100 cc. with 95% alcohol. For this purpose No. 30 denatured alcohol is satisfactory.

Diphenylcarbazide can be made by heating 50 g. of phenylhydrazine and 15 g. of urea in a flask over a flame for 4 hours up to 155°C. or until ammonia is no longer given off and by crystallization from alcohol until the crystals are no darker than straw color. As a very good grade of diphenylcarbazide may be obtained at a reasonable cost from the Organic Chemical Department of the Eastman Kodak Company, nothing is gained by making the diphenylcarbazide.

Known amounts, *e. g.*, 1, 2 and 3 cc. of the standard solution are pipetted into Nessler tubes—graduated pipets are a great convenience in this work—to which are added 5 cc. of 20% HCl and water sufficient to make the total volume of liquid in the tube up to a definite volume. The Nessler tubes used in this work made 40 cc. a convenient volume. One cc. of the diphenylcarbazide solution is now added and the mixture shaken.

The liquid in the tube at once takes on a violet color, which, even when the equivalent of only 0.000001 g. of chromium is present in the 41 cc., reaches its maximum intensity in less than 10 minutes. The color varies directly as the amount of dichromate used, a variation of as litttle as 0.5 cc. of the standard solution being easily detected.

It is a simple matter to compare the color of known amounts of the solution obtained from the ash of the fat with known amounts of the standard dichromate solution when they have reacted with diphenylcarbazide.

Experimental.—The method has been tested as follows: A definite amount of a standard potassium dichromate solution was placed in a platinum dish to which alcohol and sulfuric acid sufficient to reduce the dichromate to chromous sulfate were added and the mixture evaporated until fumes of SO_3 were obtained.

Two hundred grams of fat, known to be free from chromium, were then burned in the dish and the coke ashed. The chromium added will now be in the form of Cr_2O_3, as it is in the ash from a fat which contains chromium as a result of being treated with chromic acid, and, due to the temperature to which it has been heated, not very soluble in acids. The ash was then fused with mixed carbonates, put into solution and matched against a standard dichromate solution as above.

The very finest grades of edible fats, even when they have been filtered several times through the purest filter paper, invariably give a trace of ash which contains iron, aluminum and silica, and if the fat has been hydrogenated with a nickel catalyzer, it will, regardless of any method of purification, contain traces of nickel.

To test the effects of nickel in small amounts, the fat used contained about two parts of nickel per million, and to increase the amount of iron, silica, etc., present, in some cases, a few tenths of a milligram of fuller's earth were added with the fat.

The following table gives the results of these tests:

COMPARISON OF THE AMOUNT OF CHROMIUM FOUND BY ANALYSIS TO THAT ACTUALLY ADDED TO FATS

Grams of Chromium Added to Fat	Grams of Chromium Found by Analysis	Parts of Chromium per Million Added	Found
0.0002825	0.000275	1.41	1.38
.00013	.000112	0.56	0.51
.000565	.00055	2.83	2.75
.00036	.00041	2.00	1.80
.00028	.00025	1.40	1.25
.00006	.000058	0.30	0.29

Discussion of Results.—Although the salts of many metals, some of which are sure to be present in the ash of any fat, react with diphenylcarbazide, the chromates appear to be the only ones which give a colored reaction product in an acid solution. If care is taken to have a sufficient excess of free acid present, they either do not react or else give colorless products and even when the salts themselves are colored, for instance iron chloride, the dilution of the solutions used prevents their interfering in matching the colors.

Summary

Fats which have been treated with chromic acid usually contain traces of chromium.

Small amounts of chromium may be detected and estimated by means of diphenylcarbazide.

Small amounts of other metals, especially iron, aluminium, copper and silica which are apt to be found in the ash of fats, do not interfere in this reaction.

THE PROCTER & GAMBLE CO.,
IVORYDALE, OHIO

ACTION OF FATTY ACIDS AND OILS ON A PHOTOGRAPHIC PLATE[1]

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON

Photographers know that a developable impression can occur on a photographic plate which never has been exposed to the light. Old plates frequently show black borders after development and markings are sometimes observed on "daylight" films. The printed identification marks on the black paper of these films have been known to register themselves on the negative.

Russell[2] has demonstrated that many substances produce on a photographic plate results very similar to those produced by light. Some of the substances mentioned by Russell are magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony, wood, leaves, seeds, roots, bulbs, petals of flowers, linseed oil, olive oil, terpenes and resins. He found starch, cellulose, gum, sugar, pith, pollen and paraffin oils to be inactive.

These active substances differ widely in character but their action on the plate is apparently the same except for intensity. With some substances a developable impression can be obtained in an hour; with others 18 or 20 hours are necessary. No visible change is produced on the plate before it is developed and the development is the same as for an ordinary photograph. It is not necessary to have the substance in contact with the plate. Russell found that with some substances the action would travel through a distance of 200 mm., although in most of his experiments the plate was within several millimeters of the substance.

The object of the present investigation was to examine the photographic action of fatty oils. The photographic plate was exposed to the oil in a desiccator jar so as to preclude any possible action from fumes that might be in the atmosphere. The jar was placed in a box, which was painted black inside and provided with a tightly fitting lid, so that the dark room in which the box was placed could be entered and left without affecting the experiments. Uncovered petri dishes holding about 35 g.

[1] Presented before Am. Chem. Soc., Washington Meeting, April, 1924.

[2] Proc. Royal Inst. of Great Britain, **16,** 140 (1899–1901); Proc. Royal Soc. of London, *Biol. Sci.*, **78,** 385 (1906) and **80,** 376 (1908).

of oil, which came within two or three millimeters of the top, were used for each experiment. Pieces of white blotting paper with designs cut in them were laid across the dishes and the photographic plates were placed on top of the blotting paper.

Freshly expressed peanut, corn, cottonseed, linseed and chinawood oils produced no pictures when plates were exposed to them for 18 hours at room temperature. After these oils had been exposed to the sun for five or six hours, however, they did produce pictures of the designs cut in the blotting paper. Peanut oil produced a rather faint picture; corn and cottonseed oils, much sharper ones. When corn and cottonseed oils were used, the action went through the blotting paper and produced a dark disk on the plate. With linseed oil a very sharp picture and a dark disk were obtained. Chinawood oil produced only a faint picture. Several miscellaneous oil samples that had been in the laboratory for various lengths of time were placed with photographic plates. Perilla oil, six years old, produced a sharp picture and a faint disk; sesame oil, six months old, a faint picture; olive oil, three years old, a sharp picture and a disk; U. S. P. castor oil, a sharp picture and a dark disk; commercial coconut oil, a sharp picture and a dark disk. A sample of butterfat, which was known to be 26 years old, gave a sharp picture and a very faint disk. Commercial hydrogenated sesame oil with an iodine number of 27.2 (the iodine number of sesame oil is 110) gave no picture but after being exposed to the sun for five or six hours it produced a picture of medium intensity.

The following tests were made to determine whether there is any difference between the photographic activity of saturated and unsaturated fatty acids. Neither palmitic acid (m. p. 62.5, prepared in this laboratory) nor stearic acid (Kahlbaum) gave a picture, even after being exposed to the sun for five hours. Oleic acid (Kahlbaum) that had been kept in a brown bottle in a dark cupboard for several years, upon being placed with a plate for 18 hours gave a faint picture, but after exposure for four or five hours gave a very dark picture and disk. The sun-exposed oleic acid required only two and one-half hours to produce a medium dark image. The saturated and unsaturated acids were separated from an inactive refined cottonseed oil by the lead salt-ether method. The saturated acids gave no picture after exposure to the sun. The unsaturated acids, however, showed even more activity than the oleic acid. When placed with a plate for 18 hours, they produced a faint image before being activated by the sun and after being in the sun for five hours, a disk so black that the image was almost completely obscured. The sun-activated unsaturated acids produced a medium dark image in one and one-half hours. It is evident therefore that the photographic activity of fatty oils is connected with the unsaturated acids.

The activity of an oil or fatty acid is destroyed or greatly decreased by

heating to approximately 120° for several hours. The activity can be transferred to a certain extent. Blotting paper placed over very active oils becomes permeated with the active substance and then is capable of affecting a plate.

Russell's experiments indicate that this photographic action of certain substances is produced by a vapor rather than by any form of radioactivity. He found that the action would pass along a glass tube, even when it was bent at right angles, that it could be swept out of a tube by a slow current of air and that it did not affect an electrical field. He attributed the activity to the formation of H_2O_2 and states that all active metals have the property of producing H_2O_2 in the presence of moisture, that terpenes in the presence of moisture and air cause the formation of H_2O_2 and that every result obtained by exposing a plate to a metal or organic body can be exactly imitated by using H_2O_2. He found that a picture could not be produced in an atmosphere of CO_2.

The authors have found that an oil containing 0.0016% H_2O_2 will produce a very dark image and a medium dark disk during an 18-hour exposure and that an oil containing 0.0002% H_2O_2 will produce a medium dark image but no disk. The active substance leaves the oil slowly and whatever the nature of the substance causing the photographic action, the amount that comes off the oil during 18 hours is very small.

The following tests were made while attempting to establish the identity of this substance:

Blotting papers saturated with a solution containing KI, starch and a little $FeSO_4$ were laid across petri dishes, containing the most active oils, in desiccator jars and allowed to remain for 18 or 20 hours. Small beakers containing a few cubic centimeters of water were placed in the jars to keep the blotting papers moist. The unsaturated acids of cottonseed oil produced a reddish purple disk and the other less active oils gave fainter disks or none. Tests were made in a similar way with titanium sulfate, which is given by Treadwell and Hall as a test for distinguishing between hydrogen peroxide and ozone. In this case the unsaturated acids produced a distinctly yellow disk. The others evidently were not active enough to give a coloration. The vapor given off by cottonseed oil unsaturated acids was also tested with a blotting paper saturated with a solution containing ferric sulfate and potassium ferricyanide. At the end of 18 or 20 hours there was a blue disk on the paper showing that there had been a reduction to ferric ferrocyanide. These results are strong evidence that the active substance is hydrogen peroxide.

Summary

Russell has shown that many substances, such as certain metals, wood, leaves, roots, bulbs and resins, have the property of producing a develop-

able impression on a photographic plate when placed in proximity to it in the dark. He believed that the active substance is hydrogen peroxide. The present investigation shows that freshly expressed vegetable oils or fats do not have this property but after they have been exposed to the sun for several hours they become active. The saturated fatty acids are inactive, even after exposure to the sun. On the other hand, the unsaturated fatty acids are faintly active before exposure to the sun and after such exposure become intensely active.

Heating to approximately 120°C. for several hours destroys or greatly decreases the activity. Blotting paper placed over very active oils becomes permeated with the active substance and capable of affecting a plate.

The substance that is given off by an active oil will liberate iodine on a test paper saturated with a solution containing potassium iodide, starch and a little ferrous sulfate. It will turn a paper saturated with titanium sulfate, yellow, and a paper saturated with a solution containing ferric-ferricyanide, blue, showing that there has been a reduction to ferric-ferrocyanide.

These results confirm Russell's opinion that the substance is hydrogen peroxide.

This investigation was proposed by Dr. C. A. Browne, Chief of this Bureau, and the authors are indebted to him for many helpful suggestions.

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AN APPARATUS FOR APPROXIMATE OR COMPARATIVE MELTING POINTS OF FATS, WAXES AND PETROLEUMS

BY HOYT STEVENS

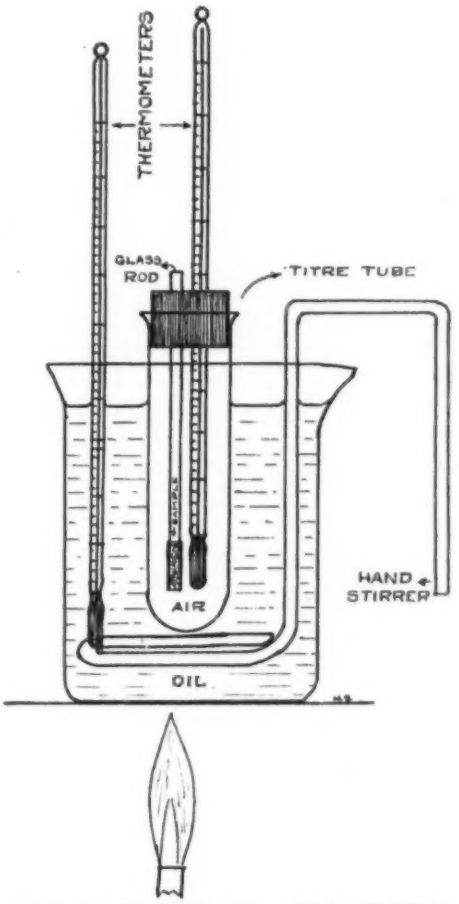
This apparatus consists of the ordinary hand-stirred melting-point bath of paraffin oil and thermometer and in addition a one inch titer tube or short test-tube equipped with a two-hole stopper which has a small groove along one side to prevent possible pressure when subjected to heat.

The holes in this stopper are bored, as nearly as possible, equal distances from the circumference of the stopper and about one-eighth inch apart. They are made to accommodate a thermometer and a glass rod (slightly smaller than the thermometer) whose bottom end is cut off square and left sharp.

The sample in case of solids such as beeswax, carnauba wax, paraffin, spermacetti, stearic acid, etc., is melted on a water bath and the bottom end of the rod dipped in about one-half inch and immediately withdrawn. By holding the rod horizontally and rotating while cooling, a uniformly thin film is produced. The small drop adhering to the bottom of the rod is scraped

off with the finger nail and both the thermometer and the rod inserted in the stopper so that they will each reach to about a half inch from the bottom of the tube.

The stopper is then put in the tube and the tube immersed in the oil which has previously been heated to a temperature ten degrees above the



MELTING POINT APPARATUS
for
FATS WAXES & PETROLATUMS

expected melting point of the sample and the flame removed. Care must be taken to get the rod and the thermometer as nearly equidistant from the sides of the tube as possible.

The film on the rod is observed until it becomes transparent and the temperature noted. This is the softening point and might be of interest.

The actual melting point is noted when the film slides down the rod and forms a hanging drop on the squared end. This usually will be noted as a melting *range* of about one degree.

Unctuous masses such as petrolatum may be gotten on the rod by merely sticking the rod in the mass and squaring off the end eliminating the preliminary melting.

The rod is cleaned when the determination is made by removing from the tube and wiping with a dry rag while the wax is still liquid.

While this method may lack in absolute accuracy somewhat, it is very satisfactory for ordinary or comparative work.

UNITED DRUG CO.,
ST. LOUIS, MO.

COCONUT EXPERIMENT STATION TO BE ESTABLISHED IN CEYLON

The "Ceylon Government Gazette Extraordinary," No. 7424 of October 14, 1924, published an ordinance to provide for the establishment of a coconut experiment station in Ceylon, says a report of Vice-Consul Mason Turner, Colombo, Ceylon, to the Department of Commerce. The purpose of this experiment station is to conduct scientific investigation of problems connected with the coconut industry and to render practical assistance, by advice and demonstrations and the inspection of plantations, of persons engaged in the coconut industry. This investigation will include in particular the growth and cultivation of coconut palms, the prevention and cure of diseases and pests, and the utilization and marketing of the products of coconut palms. The Bill provides for the management of this station by the Director of Agriculture subject to the direction of a Committee. The Committee will consist of the Director of Agriculture and not less than five or more than ten other members to be appointed by the Governor. Of the appointed members, one will be an official employed in the Colonial Treasury and the others shall be persons engaged in the coconut industry. It is proposed that the initial cost of the Station shall be met by a Government loan of Rs. 250,000 repayable with 6 per cent interest in ten equal annual installments.

OBITUARY

It is difficult to realize that Otto Hehner is gone from us. The blow is all the more severe because it was so unexpected. He was attacked by malaria and died on September 9th.

Otto Hehner was born November 25th, 1853, at Marienberg, in Nassau. His father was a judge of the High Court of Appeal in Wiesbaden, and it was doubtless this legal strain in his blood which gave him that intuitive grasp of the legal aspects of the case, which was freely acknowledged by the leaders of the English Bar, who so often met him in consultation. He was educated at Wiesbaden, studied chemistry under Fresenius until in 1873 he moved to Glasgow where he became assistant to Professor Bischof. At about the same time Ramsey was also starting his professional career also as assistant to Bischof and the association between the two young men was formed which closed only with Ramsey's life.

Among the outstanding investigations associated with his name it may be recalled that the method of analyzing beeswax, based upon the constant ratio of free cerotic acid to myricin, was first devised by Hebner in 1881 (*Analyst*, **1881,** 8, 16), and that Hubl, whose name is associated with the method, did not publish the same discovery until a few months later. The dichromate method of estimating glycerol in fats was another contribution to analytical chemistry and has long been accepted as a standard process (*Analyst*, **1888,** 12, 44), and the Hehner method of estimating the hardness in water without the use of soap solution is almost as widely known (*Analyst*, **1884,** 8, 77).

The characteristics which must have struck everyone first in dealing with Hehner were his straightforwardness, his love of justice and the simplicity of his nature. To those who did not know him well his manner might seem brusque at times, and he was inclined to be impatient with those whose brains moved more slowly than his. Yet these were only surface faults, and beneath was a deep vein of genuine sympathy. None of his friends ever turned to him in vain for counsel or help, and only those who were closely associated with him know of his many acts of kindness and generosity even to complete strangers. His outlook on life was shrewd, but never cynical, and was always instinct with a broad humanity. When the writer first knew him he was inclined to be dogmatic in the expression of his views, but time softened this and in his later years he showed a kindly tolerance of the opinions of those from whom he differed.

In his chemical work he showed that gift which is akin to genius, of seeing instinctively the crux of a problem, and he would eagerly devise ingenious methods of testing the truth of its hypothesis. At the same time he had the drawback, which is frequently part of such a temperament, of being too readily discouraged if his first efforts were unsuccessful.

Much of his time was spent in the Law Courts, and he was never happier than when he was working up the chemical side of a case and devising experiments which could be shown in Court to convince judge and jury of the truth of his contention. He was an excellent witness, clear and concise in his evidence, and always ready with a humorous answer for a cross-examining counsel.

Although in the later years of his life he was denied the happiness of the home life for which he was so well fitted, he remained unsoured, and was always ready to join in any piece of boyish fun on hand. In one of his letters to the writer he mentioned how happy he had been in his friendships throughout life. He was a lovable man, and his death makes a great and lasting gap in the lives of all of us who loved him.

C. A. MITCHELL.*

ABSTRACTS FROM OTHER JOURNALS

The recognition of hydrogenated oils. K. A. WILLIAMS, B.Sc., AND E. R. BOLTON, F.I.C. *The Analyst*, October, **1924.**—The test most widely applied for the detection of hydrogenated oils is based on the presence of traces of nickel in the oil. The evidence given by this test is confirmed by the use of certain tests of minor importance and of doubtful reliability such as microscopic examination of the crystals deposited from solutions of fat in ether. Unless nickel is found in considerable quantities the test is of little value as nowadays hydrogenated fats are manufactured free of all sub-

* From the *Analysis*, **49,** 502 (Nov., 1924.)

stances. The authors of this process for the detection of hydrogenation depend on the presence of iso-oleic acid and use mostly petroleum spirit and methylated ether in separating the salts. Petroleum ether tests lead to erroneous results. An iodine value over 5 for the spirit acids is taken as an indication of the relative amount of iso-oleic acid present. A drastic change in the composition of hydrogenated oils has recently resulted from a modification of the methods employed, by the introduction of a continuous process, whereby a flow of oil passes through a relatively large mass of catalyst. The process can be operated so as to produce (*a*) the normal proportion of iso-oleic acid in the product or (*b*) a reduced amount. It will be obvious that the control of the proportion of iso-oleic acid on a commercial scale militates against the accuracy of the deductions made from the process the use of which the authors have suggested, with the result that in cases where the method of hydrogenation employed is unknown the proportion of hydrogenated oil may be largely over-estimated. The value of the process for the actual detection of hydrogenated oil remains, however, unaltered.

Relation between the iodine values and refractive indices of hardened oils. II. H. E. WATSON AND J. J. SUDBOROUGH. *J. Indian Inst. Sci.* **7,** 81–95(1924).—Iodine values and refractive indices for oils of different degrees of hydrogenation are recorded for argemone, English mustard, rocket, Indian Rape, cashew-kernel, soya bean, poppy seed, rayan, olive, seal and cod-liver oils. Rocket, mustard and rape oils are higher refractive indices for a given iodine value than all the other oils examined except castor and argemone oils, this being attributed to the presence of glycerides of erucic acid. The high ratio of refractive index to iodine value for argemone oil is not due to glycerides of erucic acid, but to diglycerides and glycerides of hydroxy acids. The refractive index for completely hardened olive oil (n_D^{60} = 1.4463) agrees very closely with that of the purest tristearin (1.4462). Most of the curves showing the relation between iodine value and refractive index are approximately parallel, but the curve for seal oil is exceptional and crosses most of the others. Full numerical details and tables are given. (Cf. *J.*, **1923,** 103*a*.) (From *J. S. C. I.*, **43,** No. 37.) P. M.

Separation of solid saturated from liquid fatty acids. D. HOLDE, M. SELIM AND W. BLEYBERG. *Z. Deut. Öl- Fett-Ind.* **44,** 277–9(1924); *Chem. Zentr.* **95,** II, 903 (1924).—One grm. of the mixed fatty acids is dissolved in 50 cc. of 96% alcohol, neutralized with $N/2$ or $N/10$ alcoholic potassium hydroxide, diluted with the same solvent to 125 cc., and 65 cc. of water and 35 cc. of 4% thallous sulfate solution are added at the ordinary temperature. The thallous salts of the solid acids are separated by filtration through a fluted filter, and after washing, the free fatty acids are liberated from the precipitate and the filtrate by means of sulfuric acid, and determined gravimetrically after removal of the solvent. 100 g. of water dissolve 0.0461 g. of thallous oleate at 15°, and 0.3034 g. at 80°; 100 g. of 50% alcohol (by vol.) dissolve 0.0247 g. at 15%, and 100 g. of 96% by volume alcohol dissolve 2.254 g. at 15°. Excess of potassium hydroxide or of potassium soaps in presence of a small quantity of alcohol greatly increase the solubility of thallous oleate in water. (Through *J. S. C. I.*, **43,** No. 37.) P. M.

So-called polymerization of drying oils. H. WOLFF. *Z. angew. Chem.* **37,** 729–32(1924).—The change of properties of drying oils, such as linseed oil and tung oil, on heating is usually attributed to polymerization. The chief characteristics of this change are a greatly increased viscosity, some slight increase in density, and an appreciable diminution in the iodine value. In the case of linseed oil there is a considerable increase in the acid value, but this is not the case with tung oil. The increase in viscosity and the fall in the iodine value do not take place concurrently, the increase in viscosity taking place chiefly after the iodine value has fallen to a constant. Molecular weight determinations, using benzene or chloroform as solvent show some evidence of polymerization, but the results are of very little value on account of the tendency of these solvents to cause association. Intramolecular polymerization may take place between two or more unsaturated acid groups in the same molecule of glyceride, and to detect this it would be necessary to determine the mean molecular weight of the fatty acids obtained by saponification instead of the mean molecular weight of the glycerides. This was done, using camphor as a solvent, as it shows no associating power. No trace of polymerization could be detected in the fatty acids obtained from even the most highly thickened tung, linseed or soya bean oils. For example, linseed oil gave fatty acids with a molecular weight of 285, and the most highly thickened oil with a viscosity 250 times as great as that of the original linseed oil gave fatty acids with a mean molecular weight of 280. There can therefore be not more than a trace of polymerization in the process of thickening, and it is concluded that the phenomenon is actually a colloidal gelation in which at most only a small portion of the oil actually undergoes a chemical change. This is similar to the formation of a jelly by the addi-

tion of only 1% of gelatin to water. This view is supported by the fact that a large proportion of unchanged oil can be recovered from a highly gelatinized tung oil. (Through *J. S. C. I.*, **43**, No. 46.) P. M.

Polymerization of linseed oil. J. N. Friend and H. J. Alcock. *J. Oil and Colour Chem. Assoc.* **7**, 146–52(1924).—Linseed oil when heated in glass vessels in an atmosphere of nitrogen, does not undergo appreciable changes below 200°. Above this temperature there is a slight increase in density and viscosity which becomes more pronounced at about 250°. The fall in iodine value begins below 200°, but becomes more marked at 200–250°. In one sample polymerization began below 100° with prolonged heating and became very pronounced above 200°. The molecular weight determined by the freezing point of 10% benzene solutions increases somewhat as polymerization proceeds. It is necessary to use solutions of the same concentration in the molecular weight determination, as the apparent molecular weight of the oil diminishes with increased concentration of the solution, indicating combination between the oil and the benzene. (Through *J. C. S. I.*, **43**, No. 37.) P. M.

Theory of polymerization in fatty oils. II. R. S. Morrell. *J. Oil and Colour Chem. Assoc.* **7**, 153–60(1924); (cf. *J.*, **1915**, 105).—The degree of polymerization of drying oils is not accurately indicated by the determination of the iodine value, on account of the depolymerizing action of some of the components of Wijs' solution. The molecular weight of these oils cannot be satisfactorily determined with benzene as a solvent, as esters show a tendency to combine with the solvent, and association will occur if acids be present. The polymerization of linseed oil may be extra-molecular as well as intra-molecular, and it must be viewed from a colloidal as well as a strictly chemical aspect. The ethyl esters of linseed oil and of tung oil show a greater gain in weight in "drying" than do the glycerides, but the resulting films are liquid and not solid, as in the latter case, where polymerization followed by gelation takes place. There is absorption of oxygen in both cases. (Through *J. S. C. I.*, **43**, No. 37.) P. M.

Bleaching of oils and fats, a colloid chemical problem. H. T. Twisselmann. *Seifenseider-Ztg.* **51**, 351–3(1924); *Chem. Zentr.* **95**, II, 560–1(1923).—The individual components of bleaching earths, *viz.*, aluminium silicate, calcium silicate, magnesium silicate, magnesia, magnesium chloride, ferric oxide and silica showed no bleaching action, even when mixed in the same proportion as in the bleaching earths. The presence of ignited organic substances (sugar or albumin) also conferred no bleaching action on them. The bleaching action of the earths is due to their particles being electrically charged. By vigorous grinding the synthetic mixtures become electrically charged, and acquire bleaching power, and conversely active bleaching earths lose some of their activity when they are stirred with water to neutralize their electrical charges, dried at 120–150°, and then ground. Oils, therefore, should be perfectly dry when submitted to the bleaching treatment. Other physical properties, such as capillarity, surface tension and coagulation temperature of the colored substance, are of importance. The bleaching properties of the earths are improved by fine grinding. Bleaching earths containing oil are best revivified by treatment with petrol, benzene or trichloroethylene in rotary extractors. The colloidal dispersions of the earth in the mixtures of fat and solvent can be separated by the addition of a solution of salt (an oppositely charged electrolyte). (Through *J. S. C. I.*, **43**, No. 37.) P. M.

Preparation and reactivation of metallic catalysts used in the hydrogenation of oils and the like substances. Technical Research Works, Ltd., and E. J. Lush. E. P. 221,000, May 31, 1923. The fresh or spent catalyst, freed from oil, etc., is oxidized at the surface with hypochlorous acid or its salts, washed and reduced in hydrogen, the operation being preferably carried out in situ. (Through *J. S. C. I.*, **43**, No. 46.) D. G. H.

Dehydrogenating action of nickel-copper catalysts. G. Kita, T. Mazume and K. Kino. *Chem. Umschau* **31**, 165–7(1924).—Catalysts of kaolin containing 16.9% Ni and 3.1% Cu, 14.0% Ni and 6.0% Cu, and 10.5% Ni and 9.5% Cu, respectively, were used. Stearic acid at 300–310° does not undergo dehydrogenation, but unsaponifiable substances are formed, the iodine value of which increases with increase of copper in the catalyst. With herring oil, dehydrogenation of the fatty acids takes place at 200°, and at 170° with those catalysts containing more copper, and hydrogenation with those containing only nickel or nickel with a small quantity of copper. The catalyst containing little copper shows slight dehydrogenation at 100°. The temperature of reduction of the catalyst has an important effect; that reduced at 340–350° shows some dehydrogenating activity even at 100°, but that reduced at 220–230° shows none at any of the temperatures employed. (Through *J. S. C. I.*, **43**, No. 37.) M. P.

Constituents of American (Mississippi Delta) cotton wax. P. H. CLIFFORD AND M. E. PROBERT. *J. Text. Inst.* **15,** 401–13*t*(1924).—The method previously employed for extracting the wax of American cotton (Fargher and Probert, *J.*, **1923,** 263A.) was open to the objection that superheated steam was used for the heating and might cause saponification, and that the benzene used was impure. American Mississippi cotton has now been extracted with chloroform. The results obtained confirm those obtained previously, the only noteworthy error in the former results being due to the presence of impurities from the benzene in the hydrocarbon fraction. Using carbon tetrachloride as the extracting agent, the waxes obtained from the Mississippi Delta cotton (0.49%) and American Upland cotton (0.35%) had the following characteristics: m. p. 76.5°, 80.5°; d 0.976, 1.005; acid value 29, 211; saponif. value 57, 76; saponif. value after acetylation, 137, 121; acetyl value 84, 48; iodine value 27, 20; unsaponifiable matter, 68%, 66%; acetyl value of unsaponifiable matter, 123, 117. The wax of the Mississippi Delta cotton contains, therefore, a lower proportion of combined acids and a higher proportion of free alcohols than the Upland cotton. A sterol, $C_{34}H_{58}O$ (m. p. 197–199°) which does not seem to have been described previously, was isolated. None of the acid occurs in the form of soaps. (Through *J. S. C. I.*, **43,** No. 40.)

S. H. H.

Action of chlorine water on unsaturated fatty acids. A. GRUN, E. ULBRICH AND J. JANKO. *Z. Deut. Öl- Fett-Ind.* **44,** 169(1924); *Chem. Zentr.* **95,** II, 1032–3 (1924).—In accord with the observation of Margosches and Hinner (*B.*, **1924,** 341) that fats add not iodine but IOH, from iodine solutions, the authors find that a similar change occurs when chlorine acts on the unsaturated acids of fats in the presence of water. Oleic acid reacts with chloride in the presence of water and boric acid to form chlorohydroxstearic acid, iodine value 0.48. The neutralization value of the product indicates that partial formation of the anhydride occurs. The esters of oleic acid show similar behavior. The acids from marine animal oils exhibit the same properties but the tendency to form anhydride is greater. Neutral marine animal oils react in a similar manner but more slowly. (Through *J. S. C. I.*, **43,** No. 41.) F. B.

Action of halogens on unsaturated fats. J. J. CERDEIRAS. *Bull. Soc. chim.* **35,** 902–4(1924).—The comparative rates of addition of Wijs' reagent and a solution of iodine in acetic acid to substances containing ethylenic linkages has been studied. In the case of olive oil and linseed oil, Wijs' reagent is some 3–4 times more reactive than the iodine in acetic acid solution, and in the case of oleic and linolenic acids some 2–3 times as reactive. In each case the reaction with Wijs' reagent is practically complete after 40 mins. (Through *J. S. C. I.*, **43,** No. 41.) A. E. C.

Removing odoriferous substances from oils and fats. H. BOLLMANN. E. P. 218,910, Nov. 19, 1923. The fatty oil flows down a column provided with horizontal partitions and packed with Raschig rings or the like. Steam flows in counter current to the oil passing up from one compartment to the next through short tubes with hoods suspended over them. The oil accumulates in a thin layer on the partitions, is freed from water by a heating coil, and passes through overflow tubes to the next stage, there undergoing similar treatment, and so on to the bottom stage. The oil is then treated with low pressure superheated steam in a vacuum apparatus to remove the last traces of water. (Through *J. S. C. I.*, **43,** No. 42.) D. G. H.

Natural soaps in soya beans. S. MURAMATSU. *Nippon Kwagaku Kwai Shi* (J. Chem. Soc., Japan) **44,** 1035–49(1923).—The soaps contained in soya beans were extracted with warm 80% alcohol; the amount varied slightly in different species, *viz.*, from 1.44 to 1.86% on the dried material. By decomposing the soap with hydrochloric acid a mixture of fatty acids (42.22% of the total organic acids) and hydroxy acids (57.78%) was obtained. The fatty acids were separated into liquid acids (29.31% of the total acids), m. p. 38°, and solid acids (4.63%) m. p. 55°. From the latter a new acid, hispidic acid ($C_{34}H_{68}O_{17}$, white crystals, m. p. 224°, 36.93%) was isolated. It gives a hexa-acetyl derivative, m. p. 155), and its alkaline salt gives a viscous aqueous solution, which has a high foam producing and cleaning power. (Through *J. S. C. I.*, **43,** No. 42.) K. K.

Determination of fat in butter and margarine. J. GROSSFELD. *Z. Unters. Nahr. Genussm.* **47,** 420–32(1924).—Five grams of the sample are placed in a flask, 100 cc. of trichloro ethylene was added, the flask is closed with a cork and the mixture is shaken until the fat has dissolved; 5 g. of ignited calcium sulfate are then added, the mixture is again shaken, the clear solution is filtered rapidly, 25 cc. of the filtrate are evaporated in a tared flask, and the residue of fat is dried at 105–110°, and weighed. A correction is applied for the slight loss of solvent during the filtration; this correction is found by experiment with pure fat alone. (Through *J. S. C. I.*, **43,** No. 46.)

W. P. S.